



Designation: D 6481 – 99

An American National Standard

Standard Test Method for Determination of Phosphorus, Sulfur, Calcium, and Zinc in Lubrication Oils by Energy Dispersive X-ray Fluorescence Spectroscopy¹

This standard is issued under the fixed designation D 6481; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the quantitative determination of additive elements in unused lubricating oils, as shown in Table 1.

1.2 This test method is limited to the use of energy dispersive X-ray fluorescence (EDXRF) spectrometers employing an X-ray tube for excitation in conjunction with the ability to separate the signals of adjacent elements.

1.3 This test method uses interelement correction factors calculated from empirical calibration data.

1.4 This test method is not suitable for the determination of magnesium and copper at the concentrations present in lubricating oils.

1.5 This test method excludes lubricating oils that contain chlorine or barium as an additive element.

1.6 This test method can be used by persons who are not skilled in X-ray spectrometry. It is intended to be used as a routine test method for production control analysis.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations to use. (See Note 1.)*

2. Summary of Test Method

2.1 A specimen is placed in the X-ray beam, and the appropriate regions of its spectrum are measured to give the fluorescent intensities of phosphorus, sulfur, calcium, and zinc. Other regions of the spectrum are measured to compensate for varying background. If the detector does not completely resolve all the elements in a single measurement, then to improve selectivity, there is a combination of sequential and simultaneous measurements employing primary and secondary beam filters. There can be correction of measured intensities for spectral overlap. Concentrations of the elements of interest are determined by comparison of these intensities against a

TABLE 1 Elements and Range of Concentrations Determined

Element	Concentration Range
Phosphorus	0.02 to 0.3 mass %
Sulfur	0.05 to 1.0 mass %
Calcium	0.02 to 1.0 mass %
Zinc	0.01 to 0.3 mass %

calibration curve using empirical interelement correction factors and ratio to backscatter.

2.2 The EDXRF spectrometer is initially calibrated using a set of prepared standards to collect the necessary intensity data. Each calibration line and any correction coefficient are obtained by a regression of this data, using the program supplied with the spectrometer.

3. Significance and Use

3.1 Some oils are formulated with organo-metallic additives, which act, for example, as detergents, antioxidants, and antiwear agents. Some of these additives contain one or more of these elements: calcium, phosphorus, sulfur, and zinc. This test method provides a means of determining the concentrations of these elements, which in turn provides an indication of the additive content of these oils.

3.2 This test method is primarily intended to be used at a manufacturing location for monitoring of additive elements in lubricating oils. It can also be used in central and research laboratories.

4. Interferences

4.1 The additive elements found in lubricating oils will affect the measured intensities from the elements of interest to a varying degree. In general, for lubricating oils, the X-radiation emitted by the element of interest can be absorbed by itself (self-absorption) or by the other elements present in the sample matrix. Also the X-radiation emitted from one element can further excite (enhance) another element. These interelement effects are significant at concentrations varying from 0.03 mass %, due to the heavier elements, to 1 mass %, for the lighter elements. Enhancement effects can be minimised by selective excitation. The measured concentration for a given element can be mathematically corrected for self-absorption

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

Current edition approved Nov. 10, 1999. Published January 2000.